

# A Novel Route for the Preparation of Hybrid Zwitterionic Membranes Containing Both Sulfonic and Carboxylic Acid Groups

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**ABSTRACT:** A novel route for the preparation of hybrid zwitterionic membranes containing both sulfonic and carboxylic acid groups is reported. Based on this synthetic methodology, a series of membranes were synthesized via sol-gel reaction, zwitterionization process, and the oxidation of the -SH group. FTIR spectra confirmed the corresponding reactions. The properties of these prepared membranes were characterized by ion-exchange capacity (IEC), water content, and pure water flux, etc. The anion-exchange capacity (AIEC), total cation-exchange capacity (CIEC<sub>total</sub>), and the CIEC of the sulfonic groups (CIEC<sub>sulf</sub>) of the membranes coated for 1–3 times were in the range of 0.017–0.12, 0.1–0.53, and 0.029–0.14 mmol g<sup>-1</sup>, respectively. The mea-

surement of water content showed that it was independent of pH values whether for the membranes coated once or twice. Pure water flux revealed a downward trend with the increased coating times. The surface SEM images of the produced membranes exhibited that these membranes' textures could be affected highly by the curing temperature, and excessively higher curing temperature would lead the membranes to brittle and chasm. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 107: 3033–3041, 2008

**Key words:** zwitterionic membrane; hybrid membrane; ion-exchange membrane; mercapto group; 3-(mercapto-propyl) trimethoxysilane

## INTRODUCTION

With the rapid development of modern industry, more and more industrial wastes have ruthlessly polluted the natural environment. Meanwhile, public attention for environmental protection is rapidly escalating. Thus the treatment of industrial wastewater and the recovery of wasted chemicals become extremely important. With the drive to treat such environmentally harmful species, innovative technologies to meet this demand have attracted numerous researchers. Because it provides such advantages as lower operation expense, secure process, and mature technology support,<sup>1–4</sup> an ion-exchange membrane has become one of the most promising technologies

and found many applications in modern industries. For example, ion-exchange membranes have been widely used for the desalination of seawater, the treatment of wastewater, and the removal of salts from aqueous solutions.<sup>4,5</sup> In view of its significance, the researches for such membrane technology therefore are turned into especially significant, which is the reason for the high interests in these types of membranes.

At present, many efforts are made to develop ion-exchange membranes.<sup>5,6</sup> Among them, inorganic-organic hybrid membranes are becoming more attractive.<sup>6,7</sup> The main advantageous properties of these membranes are their structural flexibilities, thermal and mechanical stabilities when compared with the polymeric ones.<sup>1,7–9</sup> Also, the disadvantages of those organic membranes are being experienced with their utilizations in industry processes. For example, it is reported that polymeric membranes bearing sulfonic acid groups exhibited some demerits,<sup>10</sup> such as excessive water swelling, weak mechanical strength, and poor permselectivity, etc., and it is suggested that the membrane containing both sulfonic and carboxylic acid groups can be considered as an alternative one. For this reason, it is necessary to develop new techniques to prepare such type of membrane and overcome its demerits as cited earlier.

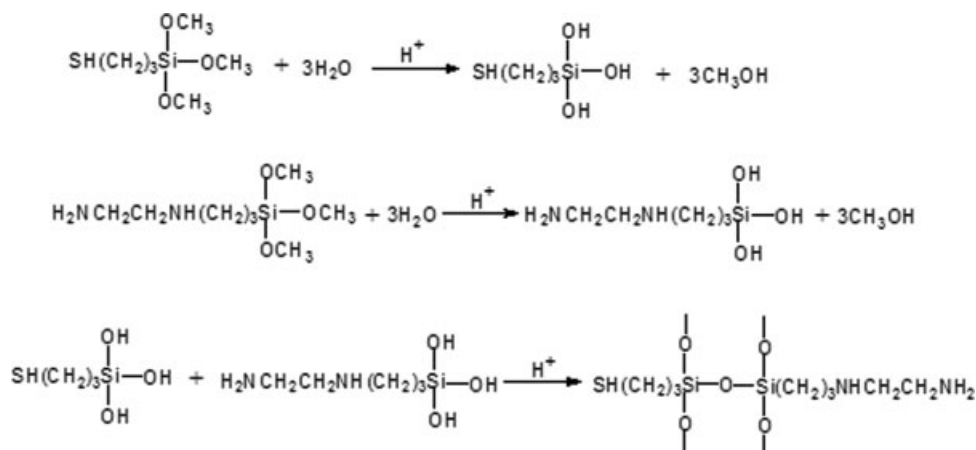
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**Scheme 1** Hydrolysis and condensation reaction of *N*-[3-(trimethoxysilyl)propyl] ethylene diamine (TMSPEDA) and 3-(mercaptopropyl) trimethoxysilane (MPS). Hydrolysis reaction (complete hydrolysis is shown for simplicity); Condensation reaction (non stoichiometric balance).

Recently, in our laboratory, an earnest attempt has been made to synthesize and characterize hybrid charged membranes or materials.<sup>11–14</sup> To develop novel ion-exchange membranes, inorganic–organic hybrid zwitterionic polymers and membranes have also been prepared and characterized in our laboratory.<sup>15–17</sup> These hybrid zwitterionic membranes were synthesized successfully via sol–gel reaction and zwitterionic process to create ion pairs grafted on the polymer chains.<sup>18,19</sup> Our continuing interest in such types of membranes stimulates us to develop new route for their preparations. Therefore, to continue the previous researches and have an insight into the effects of different acidic groups on the membrane's performances, a new route for the preparation of hybrid zwitterionic membranes containing both sulfonic and carboxylic acid groups is initiated in this article. Hopefully, such membranes are suitable for the desalination of brackish water and the removal of salts from aqueous solutions. Compared with the membranes reported previously,<sup>15–17</sup> particular attention should be paid to this novel synthetic method, in which the membranes were prepared via a coupling reaction between the 3-(mercaptopropyl) trimethoxysilane (MPS) and *N*-[3-(trimethoxysilyl)propyl] ethylene diamine (TMSPEDA), and subsequent process of the zwitterionization and the oxidation of the –SH group.

## EXPERIMENTAL

### Materials

*N*-[3-(trimethoxysilyl)propyl] ethylene diamine (TMSPEDA) (purity: > 95.0%) and 3-(mercaptopropyl) trimethoxysilane (MPS) (purity: > 95.0%) were purchased from Silicone New Material of Wuhan University (Wuhan City, China) and used without further purification. 1,4-Butyrolactone (BL) (purity: >

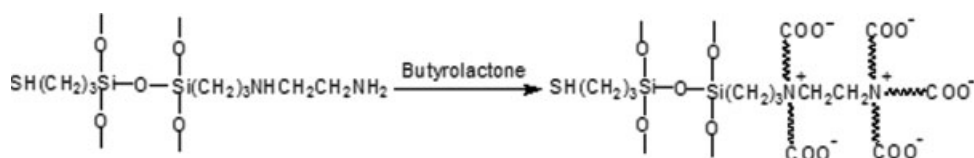
97.0%) and other reagents (of analytical grade) were purchased from Shanghai Chemical Reagent (Shanghai City, China) and used as received. Microporous alumina plates were obtained from ZiBo Ceramic Institute of Shandong (ZiBo City, Shandong Province, China), and they had a symmetrical structure with porosity 40–45%, average pore diameter around 0.027 μm, and the total thickness about 0.5 cm.

### The preparation of hybrid zwitterionic membranes

The possible reactions for the preparation of hybrid zwitterionic precursors are illustrated in Schemes 1–3. The reactions in Scheme 1 are the hydrolysis and condensation of TMSPEDA and MPS. The crosslinking reaction between the prepared hybrid precursor and the 1,4-butyrolactone (BL) is exhibited in Scheme 2. In Scheme 2, the BL opened the lactone ring and reacted with the –NH– groups of the hybrid precursor, resulting in the creation of ion pairs grafted on the two sides of the polymer chains, which exhibited a pendent side chain structure; this is due to its secondary amine features.<sup>16,17</sup>

To prepare a hybrid zwitterionic membrane containing both sulfonic and carboxylic acid groups, the microporous alumina plate was immersed in the coating solution whose chemical compositions are listed in Table I. After immersing for 15 min, the alumina plate was air-dried at room temperature (near 28°C) for 30 min, kept at 70°C for 1 h, and allowed to cool off to room temperature; it was then cured at the specified temperatures for additional 1 h. Finally, this membrane was immersed in an aqueous H<sub>2</sub>O<sub>2</sub> solution (30%, wt) to oxidize the mercapto group for additional 6 h so as to produce –SO<sub>3</sub>H in the developed membrane (Scheme 3).<sup>13,20</sup>

Moreover, it is interesting to find that the unpleasant odor derived from the –SH group was elimi-



**Scheme 2** Zwitterionic process of the prepared hybrid precursors to create ion pair grafted on the polymer chain (complete reaction is shown for simplicity).

nated gradually with the oxidation proceeding; and the color of the membranes cured at 100, 150, and 200°C changed from white, yellow to brown, respectively. After the completion of the oxidization of the —SH group, the corresponding membranes were rinsed sufficiently with the deionized water to remove the excess H<sub>2</sub>O<sub>2</sub>. The above steps were repeated several times for the same alumina plate to increase the membrane's thickness. The final membranes cured at 100, 150, and 200°C were denoted as membranes A, B, and C, respectively.

In addition, it should be noted that to demonstrate the reproducibility of the preparation procedures, for each temperature, three samples were prepared at the identical conditions and the final properties were averaged from the measurements of these three identical membranes.

### Membrane characterizations

FTIR spectra of the films obtained from the explored samples were recorded with a Bruker Equinox-55 FTIR spectrometer in the range of 4000–400 cm<sup>-1</sup> with a resolution of 0.5 cm<sup>-1</sup>.

The effective membrane area for the measurements of both the anion-exchange capacity (AIEC) and the cation-exchange capacity (CIEC) were about 21.6 cm<sup>2</sup>. The AIEC of the synthesized membranes was determined using the Mohr method, in which the membranes were converted to Cl<sup>-</sup> ionic forms with an aqueous NaCl solution (0.1 mol dm<sup>-3</sup>), and back titrated with an aqueous AgNO<sub>3</sub> solution (0.01 mol dm<sup>-3</sup>), which was standardized by NaCl reference reagent dried at 300°C for 2 h; and this AIEC was expressed as mmol g<sup>-1</sup>-dry membrane.<sup>2</sup> The CIEC of these membranes was determined by the similar way, in which the membranes were converted to Na<sup>+</sup> ionic forms with an aqueous NaOH solution (0.01 mol dm<sup>-3</sup>), and back titrated with an aqueous HCl solution (0.01 mol dm<sup>-3</sup>), which was

standardized via Na<sub>2</sub>CO<sub>3</sub> reference reagent dried at 260°C for 1 h, and the CIEC was expressed as mmol g<sup>-1</sup>-dry membrane.<sup>16,17</sup> Because of these membranes bearing both strong and weak acid groups (i.e., —SO<sub>3</sub>H and —COOH groups), the CIEC was thus determined by two steps as follows:

**Step 1.** The total amount of cation-exchange capacity including both sulfonic and carboxylic acid groups in the prepared membranes, CIEC<sub>total</sub> [CIEC<sub>total</sub> = CIEC ((—SO<sub>3</sub><sup>-</sup>) + (—COO<sup>-</sup>))], mmol g<sup>-1</sup>) was determined using the method mentioned earlier,<sup>16,17</sup> in which the membranes were converted to Na<sup>+</sup> ionic form, then back titrated with 0.01N HCl solution.

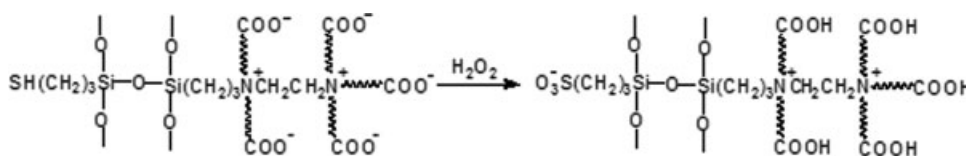
**Step 2.** The CIEC of the sulfonic groups in these membranes, CIEC<sub>sulf</sub> was determined according to the cationic substitute technique. The prepared membrane (in the H<sup>+</sup> ionic form) was immersed in an aqueous Na<sub>2</sub>SO<sub>4</sub> solution (0.1 mol dm<sup>-3</sup>) for 24 h to replace H<sup>+</sup> by Na<sup>+</sup> ions; then titrated with an aqueous NaOH solution (0.01 mol dm<sup>-3</sup>), which was standardized previously via KHC<sub>6</sub>H<sub>4</sub>(COO)<sub>2</sub> reference compound dried at 110°C for 1 h; the CIEC<sub>sulf</sub> could thus be computed based on the amount of H<sup>+</sup> ions exchanged by Na<sup>+</sup> ions in the sulfonic groups.

The measurement of pure water flux (*F*) was carried out in a self-made dead-end membrane module as described in detail in a previous article.<sup>21</sup> The pressure difference used in this testing was around 0–1.5 MPa, and the effective membrane area was about 18.5 cm<sup>2</sup>. The total volume of the water across the membranes was collected at a given time interval (1–10 min). To reduce the experimental errors, the mean values of three times testing for each tested membrane were selected as its final result. The data of pure water flux can be calculated from  $F = V / (At\Delta P)$ , where *V* is the total volume of water permeated the membranes; *A* represents the membrane area; *t* denotes the operation time; and  $\Delta P$  is the pressure difference across the tested membranes.

The determination of water content (*W<sub>R</sub>*) in the membrane was conducted using conventional process,<sup>2,16,17</sup> in which water content in the membrane was calculated from the difference of the wet and the dried membrane, i.e.,  $W_R = (W_{\text{wet}} - W_{\text{dry}}) / W_{\text{dry}}$ , where the *W<sub>wet</sub>* and *W<sub>dry</sub>* are the weight of the wet and the dried membrane, respectively. The wet

**TABLE I**  
Compositions for the Hybrid Zwitterionic Membranes

MPS (mol)	TMSPEDA (mol)	BL (mol)	BuOH (mol)	CH <sub>3</sub> COOH (mol)
0.1	0.1	0.4	0.4	0.001



**Scheme 3** The oxidization of the mercapto ( $-\text{SH}$ ) group to produce negatively charged sulfonic acid group in the above-prepared membranes.

membrane was prepared by immersing the dried one in deionized water for 2 h, then taken out, swept the surface water with filter paper, and weighed instantly. The pH values of the deionized water were adjusted with an aqueous HCl or KOH solutions ( $0.1 \text{ mol dm}^{-3}$ ).

The above measurements such as the IECs, pure water flux, and water content, etc, were conducted at room temperature (near  $28^\circ\text{C}$ ).

Scanning electron microscopy (SEM) images of these prepared membranes were observed by an XL30-ESEM environmental scanning electron microscope (Philips), operated with an accelerating voltage of 20.0 kV and magnification times of  $1000\times$ .

## RESULTS AND DISCUSSION

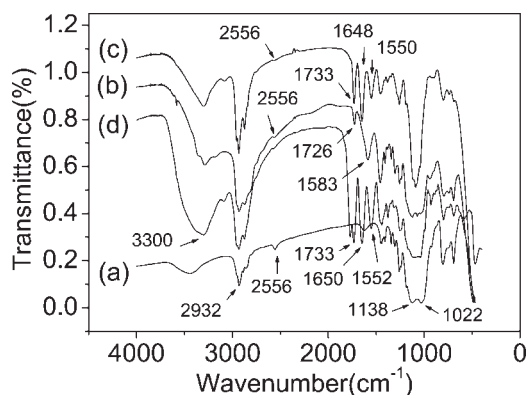
### FTIR spectra

To demonstrate the reactions described in Schemes 1–3 and investigate the bonding coupling behaviors of the prepared samples, FTIR spectroscopy was conducted and shown in Figure 1(a–d).

As can be seen in Figure 1(a), the distinct absorption peak at  $2550\text{--}2600 \text{ cm}^{-1}$  was in the region of  $-\text{SH}$  group stretching<sup>13,20</sup>, while the peak at around  $1100 \text{ cm}^{-1}$  was the  $-\text{Si}-\text{O}-\text{C}$  stretching from trimethoxysilane groups of MPS.<sup>13</sup> The strong absorption peaks associated with  $-\text{CH}_3$  or  $-\text{CH}_2-$

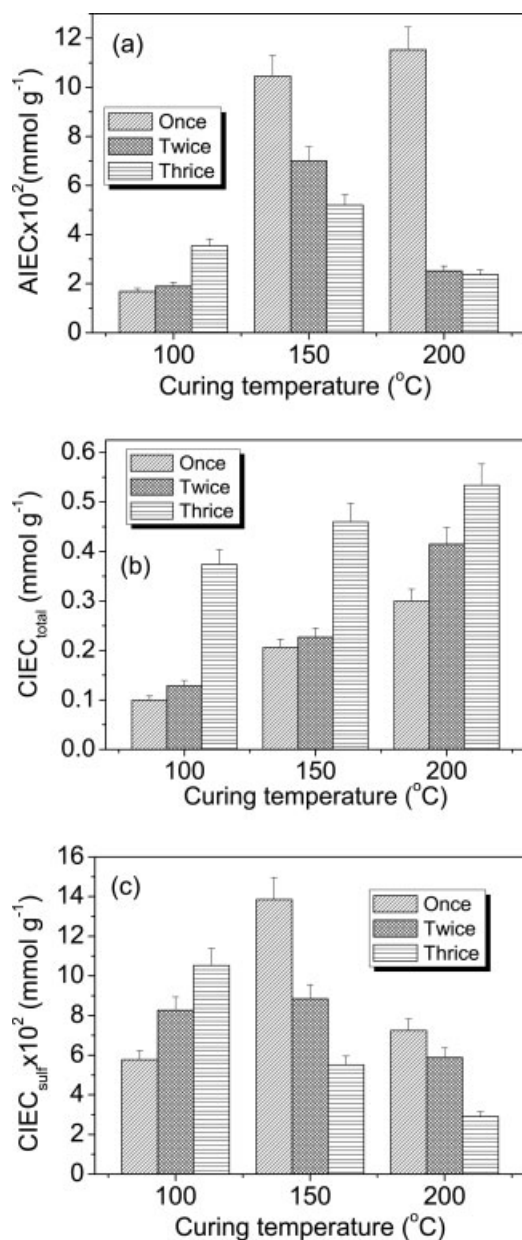
groups were observed at  $2930 \text{ cm}^{-1}$ . The peak located at near  $1458 \text{ cm}^{-1}$  was the scissors and asymmetric vibration of  $-\text{CH}_3(\text{vs})$  or  $-\text{CH}_2-(\text{vs})$  of MPS, which was likely contributed by the  $-\text{SH}$  group.<sup>22</sup> The peak situated at  $810 \text{ cm}^{-1}$  (unmarked in the spectrum) should be assigned to the  $\text{C}-\text{S}$  stretching.<sup>23,24</sup> In Figure 1(b), it can be found that the new band appeared at  $1583 \text{ cm}^{-1}$  was the  $\text{N}-\text{H}$  bond stretching vibration and asymmetric deformation,<sup>21</sup> and the broad peak at near  $1100 \text{ cm}^{-1}$  was related to the  $-\text{Si}-\text{O}-\text{Si}$ ,  $-\text{Si}-\text{O}-\text{C}$ , and  $-\text{C}-\text{O}-\text{C}$  stretching<sup>13,20,25</sup>; these changes in the absorption peaks proved the occurrence of the reactions described in Scheme 1. Meanwhile, the peak situated at  $1726 \text{ cm}^{-1}$  should be attributed to the stretching vibration of  $\text{C}=\text{O}$  groups in  $\text{CH}_3\text{COOH}$  because of the blend of acetic acid and solvent BuOH (as listed in Table I). Furthermore, as presented in Figure 1(c,d), the new bands at  $1550$  and  $1650 \text{ cm}^{-1}$  were the asymmetric stretching vibration of  $\text{COO}^-$ ,<sup>26</sup> which supported the reaction described in Scheme 2.

In addition, it should be noted from Figure 1(c,d) that the  $-\text{SH}$  group located at  $2550\text{--}2600 \text{ cm}^{-1}$  seems to be slightly weaker in intensity and was obscure in the spectrum compared with that observed in Figure 1(a,b). This can be interpreted as the partial oxidation of the  $-\text{SH}$  group in the air, thus decreased its intensity. Such partial oxidation, however, should not give rise to much influence on the membrane's properties, because the oxidation of the  $-\text{SH}$  group is the final objective and it also can not damage the structure of the hybrid precursors. Also, the oxidization of the  $-\text{SH}$  group gives an indirect evidence for the existence of the sulfonic acid groups from the ion-exchange capacity (IEC) measurements [see Fig. 2(c), hereinafter], thus indirectly proves the reaction described in Scheme 3. In Figure 1(d), the peak shape in the range of near  $1040 \text{ cm}^{-1}$  became very broader, this is because of the overlapping of the absorption band assigned to  $-\text{SO}_3\text{H}$  in the range of  $1030\text{--}1090 \text{ cm}^{-1}$ <sup>13,20</sup> with those of  $-\text{Si}-\text{O}-\text{Si}$  and  $-\text{Si}-\text{O}-\text{C}$  stretching vibration. Moreover, the broad peak at around  $3300 \text{ cm}^{-1}$  in Figure 1(a–d) is probably because of the  $-\text{OH}$  stretching from the uncondensed  $-\text{SiOH}$  groups in the gel of MPS and the hybrid film as reported.<sup>13,20</sup>



**Figure 1** The FTIR spectra of (a) the gel of MPS, (b) the film of the resulting product of TMSPEDA and MPS, (c) the film of the zwitterionized hybrid precursor, (d) the film of the oxidized hybrid product. To avoid the large overlapping of absorption peaks, the data in spectra (b) and (c) were magnified 1.3 and 1.5 times, respectively.





**Figure 2** The effect of curing temperature on the AIEC (a), the CIEC<sub>total</sub> (b), and the CIEC<sub>sulf</sub> (c) of the prepared membranes.

### Ion-exchange capacity

To further corroborate the reactions described in Schemes 2 and 3 and probe the effects of the curing temperature on the electrical properties of the synthesized membranes, the IECs for both positively and negatively charged groups (including both strong and weak acid groups, —SO<sub>3</sub>H and —COOH) were determined and presented in Figure 2(a–c).

It can be seen that the anion-exchange capacity (AIEC) of the three types of hybrid zwitterionic membranes was in the range of 0.017–0.12 mmol

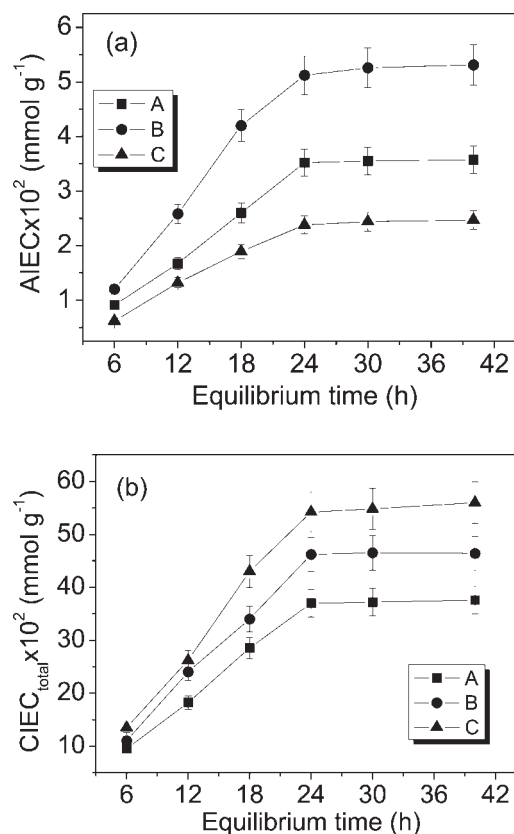
g<sup>-1</sup>, suggesting that these synthesized membranes possessed anion-exchange groups. Whereas the total cation-exchange capacity (CIEC<sub>total</sub>) of these membranes was in the range of 0.1–0.53 mmol g<sup>-1</sup>, implying that they also contained cation-exchange groups; and the CIEC of the sulfonic groups (CIEC<sub>sulf</sub>) was in the range of 0.029–0.14 mmol g<sup>-1</sup>. These findings clearly revealed that the tested membranes were able to exhibit the natures of both positively and negatively charged groups, further confirming the reactions illustrated in Schemes 2 and 3, i.e., the opening of the lactone ring in BL and the oxidation of the —SH group had occurred during the membrane preparation.

Moreover, it is interesting to find that both the AIEC and the CIEC<sub>total</sub> were affected highly by the curing temperature. As shown in Figure 2(a,b), when the membranes were coated for once, both the AIEC and the CIEC<sub>total</sub> increased with the elevated curing temperature. However, when the membranes were coated for twice or thrice, the CIEC<sub>total</sub> exhibited an upward trend with the increased curing temperature [as illustrated in Fig. 2(b)]. Nevertheless, the AIEC increased with the elevated curing temperature up to 150°C; after this curing temperature, they decreased obviously, i.e., they obtained the maximal values at 150°C [cf. Fig. 2(a)]. These behaviors can be interpreted as follows. First, when the membranes were coated once, the unhydrolyzed hybrid precursor might continue to hydrolyze and condense with the elevated curing temperature, resulting in more ion pairs being grafted on the polymer chains. The contents of both the anionic and cationic groups in the membranes will thus be promoted. The AIEC and CIEC<sub>total</sub> will increase accordingly. When the membranes were coated twice or thrice, because of more material being deposited from one coating to another, the ion-exchange ability will be enhanced; therefore the CIEC<sub>total</sub> increased with the increased coating times as expected [see Fig. 2(b)]. However, the AIEC decreased with the increased coating times at higher temperature (above 150°C) [cf. Fig. 2(a)]. The reason might be related to the curing temperature of the membranes and the coating times. At low curing temperature such as 100°C, the hydrolysis of hybrid precursor might be incompletely conducted; an increase in coating times does not significantly affect the structure of the membranes. AIEC is mainly dependent on the coating times as mentioned earlier. But at higher temperature such as 150°C, the hydrolysis and crosslinking of hybrid precursor is relatively complete. At this time, the membrane's structure will play a decisive role in AIEC. With an increase in coating times, the membrane's structure becomes tighter and denser as evidenced by SEM images in Figure 5(d–f), hereinafter. As mentioned in "Experimental" section, all the measurements for

AIEC were conducted at identical conditions, so a tighter structure will cause incomplete ion exchange. This may be one of the reasons why the AIEC decreases with an increase in coating times at higher temperature. Second, the increased Coulombic repulsion between the ion pairs in the polymer chains will also be responsible for such change trend.<sup>27,28</sup> This is because the negatively charged groups are located on the pendent side chains and the terminal of the polymer chain (cf. Scheme 1–3), which will prevent the combination of the free exchange anion such as  $\text{Cl}^-$  with the positively charged groups (quaternary ammonium groups) positioned in the main chain of the hybrid precursors. When the membrane was coated for once, the deposited material is smaller; therefore the Coulombic repulsion is relatively weaker. Whereas when the membrane was coated for twice or thrice, more material was deposited from one coating to another as mentioned earlier; consequently, the Coulombic repulsion increases with the increased coating times, leading to a decreasing trend in AIEC. Third, the change tendency in AIEC is possibly related to the inadequate equilibrium time or equilibrium times during the titration. As a result, the free ions on the ion-exchange groups might be exchanged insufficiently because of the inadequate equilibrium time or equilibrium times, particularly for the tighter and denser membranes; the AIEC will be thus lower than its actual data.

To verify the above conjecture, the dependence of equilibrium time on both the AIEC and  $\text{CIEC}_{\text{total}}$  of the tested membranes coated for thrice was determined and shown in Figure 3(a,b). It can be noted that both the AIEC and the  $\text{CIEC}_{\text{total}}$  enhanced with the increased equilibrium time, indicating an upward trend in ion-exchange ability. This finding suggests that the IECs are dependent on the equilibrium time during the titration, corroborating the conjecture made earlier. Therefore, it can be concluded that the equilibrium time is one of the primary impact factors on the IECs of the tested membranes. Furthermore, it can also be noted in Figure 3(a,b) that when the equilibrium time was beyond 24 h, the IECs increased slightly and approached a constant value, demonstrating the completion of the ion exchange. This result implies that 24-h equilibrium time is sufficient for the ion exchange conducted on the ion-exchange sites in this case.

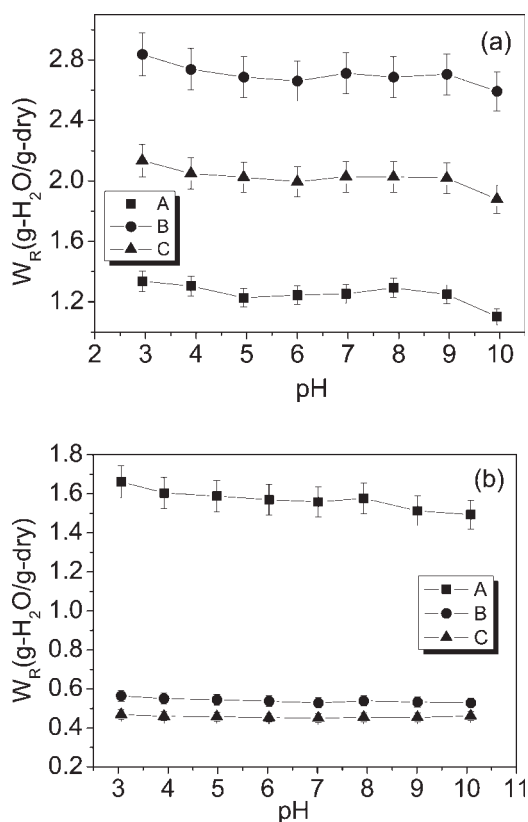
In addition, the impact of the curing temperature on the  $\text{CIEC}_{\text{sulf}}$  can be easily found in Figure 2(c). As presented in Figure 2(c), when the membranes were coated for once or twice, the  $\text{CIEC}_{\text{sulf}}$  exhibited the maximal values at 150°C. When the membranes were coated for thrice, however, it revealed a downward trend. The primary reason can be ascribed to the decrease in the rate of mass transfer to the ion



**Figure 3** The dependence of equilibrium time on both the AIEC (a) and  $\text{CIEC}_{\text{total}}$  (b) of the investigated membranes coated for thrice. A, B, and C denoted the membranes cured at 100, 150, and 200 °C for additional 1 h, respectively.

exchange sites. Meanwhile, the insufficient oxidation of the  $-\text{SH}$  group might also be responsible for this behavior. This is because when more material was deposited on the surface and pore walls with the promotion of the coating times, the membrane thickness increased accordingly; thus the rate of mass transfer was decreased because of the shrinkage of the membrane pore size. At the same time, the oxidation of the  $-\text{SH}$  group interior the portion of the membranes was thus prohibited or reduced, i.e., the oxidation of the  $-\text{SH}$  group primarily occurred on the membrane's surface and the pore walls; whereas the portion inside the membrane's surface maintained intact or was oxidized partially. As a result, the amount of the sulfonic group decreased with the increased coating times, leading to a decline trend in  $\text{CIEC}_{\text{sulf}}$ . Furthermore, the lower data of  $\text{CIEC}_{\text{sulf}}$  at 200°C is possibly related to the excessively high curing temperature, which might conduce to the partial degradation of the sulfonic group.

It should be emphasized that the data of AIEC were lower than those of  $\text{CIEC}_{\text{total}}$  and  $\text{CIEC}_{\text{sulf}}$  [as shown in Fig. 2(a–c)]. It is difficult to explain this phenomenon extensively within the authors' present



**Figure 4** Water content ( $W_R$ ) of the prepared hybrid zwitterionic membranes at different pH values, (a) coated for once; (b) coated for twice. A, B, and C were the membranes cured at 100, 150, and 200 °C for additional 1 h, respectively.

knowledge. The possible reason is related to the impact of strong acid group;  $-\text{SO}_3^-$  on membrane's performance, i.e., the exchanged ion such as  $\text{Cl}^-$  is highly rejected by  $-\text{SO}_3^-$  because of its strong dissociation effect, bringing about a decrease in AIEC of the studied membranes.

#### Water content ( $W_R$ ) in relation with pH values

For verifying the hydrophilicity of the hybrid zwitterionic membranes in various pH values, water content was determined and illustrated in Figure 4(a,b).

It can be observed that the water content ( $W_R$ ) decreased slightly with the elevated pH values whether for the membranes coated for once [see Fig. 4(a)] or twice [Fig. 4(b)]. Meanwhile, for the same pH, the water content showed different change trends with the elevated coating times [cf. Fig. 4(a,b)]. For example, for membrane A, the water content enhanced with the increased coating times; however, for membranes B and C, the water content decreased with the increased coating times. The change trend in water content with the elevated pH seems to present a falling tendency in Figure 4; but

if the experimental error is considered, this downward trend is unnoticeable, suggesting that there exists a slight effect of pH on the water content, i.e., the water content is independent of pH values whether for the membranes coated for once or twice.

Moreover, the effect of the curing temperature on the water content is capable of being obtained easily by comparing the membranes A–C coated once or twice. As shown in Figure 4(a), when the membranes were coated once, the water content decreased with the order of membranes  $B > C > A$ ; while in the case of twice coating, the water content decreased with the order of membranes  $A > B > C$ , i.e., the water content reduced with the increased curing temperature [see Fig. 4(b)]. The rational interpretation of these trends is that when the membranes were coated once, the unhydrolyzed hybrid precursors might continue to hydrolyze and condense with the increased curing temperature, leading to more acidic groups being grafted on the polymer chain as discussed earlier, thus increased the hydrophilicity of the prepared membranes. This finding is in agreement with the observation as shown in Figure 2(c): in which it is found that the membrane B has the maximal values of  $\text{CIEC}_{\text{sulf}}$  among the produced membranes in the case of once coating, hence it has the maximal water content. However, when the membranes were coated for twice, because of an increase in the amount of the deposited polymer, the oxidation of the  $-\text{SH}$  group inside the membranes was possibly conducted partially, the hydrophilicity of per unit weight of the dry membrane was thus lessened, which also made some contributions to the alteration of the water uptake; the water content therefore reduced with the increased curing temperature.

#### Pure water flux

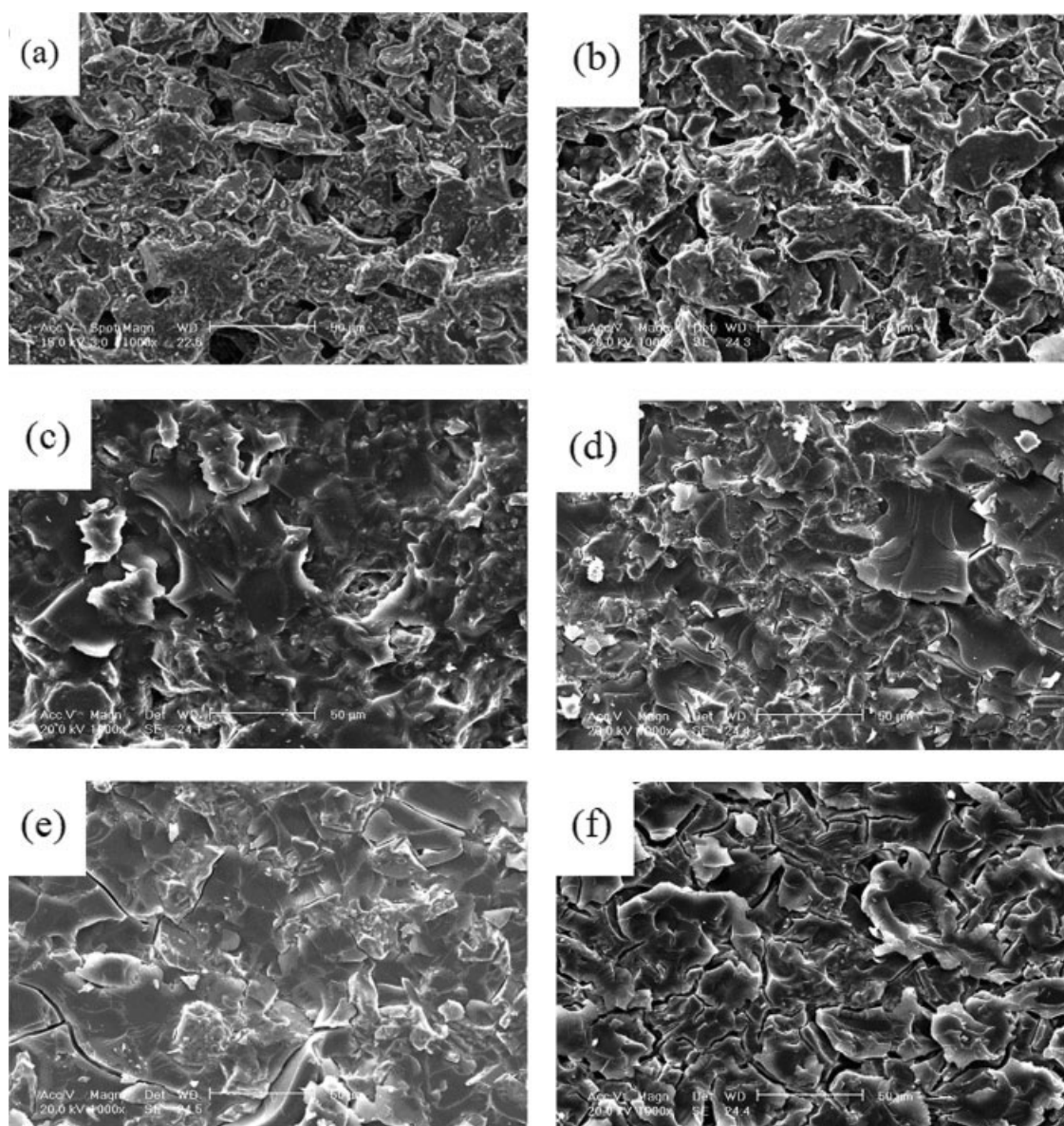
To examine the microstructure of the considered membranes and have an insight into the impacts of curing temperature on the water flux of the investigated membranes, pure water flux was measured and the corresponding results are summarized in Table II.

**TABLE II**  
Pure Water Flux [ $\text{l (m}^2 \text{ bar h)}^{-1}$ ] of the Membranes A–C Coated for Different Times<sup>a</sup>

Number of coating	Membrane A	Membrane B	Membrane C
Without coating	25,700	25,550	24,917
1	2,674	11.68	910
2	2,371	0.81	1.66
3	1,681	0.54	1.50

<sup>a</sup> Membranes A, B, and C were the membranes cured at 100, 150, and 200 °C, respectively.





**Figure 5** Surface SEM images of (a) the naked alumina plate (without coating), (b–d) membranes A–C coated for once, respectively; (e, f) membrane C coated for twice and thrice, respectively.

It is interesting to find that both the curing temperature and the coating times are capable of affecting the pure water flux of the tested membranes. As shown in Table II, for the same curing temperature, the pure water flux reduced considerably with the increased coating times. The primary cause of this trend might be assigned to both the increase in the membrane thickness and the shrinkage of the membrane pore size with the elevated coating times. However, for the same coating, the water flux decreased with the elevated curing temperature up to 150°C. After this temperature, the water flux increased a little (e.g., membrane C as listed in Table II). The possible reason is that higher curing temperature favors the formation of higher crosslinking degree of the membranes, resulting in the mem-

branes becoming tighter and denser, as well as the shrinkage of the membrane pore size; the water flux thus decreases as observed in membrane B. Nevertheless, excess high curing temperature might result in the membranes becoming brittle and crack [see the SEM images in Fig. 5(e,f) hereinafter], accordingly give rise to an increase in the water flux of the membranes cured at 200°C (as tabulated in Table II).

#### Morphology of the hybrid charged membranes

For detecting the microstructure difference in the membranes A–C coated with various times, surface SEM observations were conducted and presented in Figure 5(a–f).



It can be observed that for the same coating, the surface micrograph of the membrane A exhibited some large pores and voids [cf. Fig. 5(b)]; whereas the surface photos of the membranes B and C became denser [Fig. 5(c,d)], implying that the crosslinking degree of the membranes A–C increased with the elevated curing temperature. Compared with the large cavities observed in the naked alumina plate (without coating) [as presented in Fig. 5(a)], it is suggested that the prepared membranes have deposited on the surface of the naked alumina plates. Meanwhile, there exist some appreciable distinctions among the membranes' microstructures.

The differences in the surface morphologies of the explored membranes can be attributed to the effect of the curing temperature on the microstructure of these membranes. Considering membrane A, because of the lower curing temperature, its crosslinking degree is relatively lower, thus only small amount of thin film can be generated on the alumina plate, such film insufficiently covered the pores and voids on the surface of the alumina plate, hence its SEM image indicates the original morphology of the alumina plate [Fig. 5(a,b)]. Whereas for membranes B and C, their crosslinking degree increase with the elevated curing temperature; as a result, thicker film is produced and the thickness of such film enhance with an increase in coating times, accordingly, the membrane surface become denser, resulting in the shrinkage of the membrane pore size. In addition, when the curing temperature increases further, the crosslinking degree of these membranes also enhances, thus more inorganic moiety might be incorporated into the organic one. However, excess inorganic moiety incorporated into the organic network might cause the phase separation<sup>17</sup> and an increase in membrane pore size as reported<sup>20</sup>: the incorporation of more silica in the membrane matrix will lead to an increase in pore volume. This is possibly one of the reasons why membrane C showed marked cracks as presented in Figure 5(e,f), especially when it is coated several times. This outcome is also confirmed by the measurement of water flux in the membrane C (cf. Table II).

## CONCLUSIONS

A novel route to the hybrid zwitterionic membranes containing both sulfonic and carboxylic groups is initiated via the zwitterionization and oxidization process. The hybrid precursor for the membranes was obtained by a coupling reaction between the *N*-[3-(trimethoxysilyl)propyl] ethylene diamine (TMSPEDA) and 3-(mercaptopropyl) trimethoxysilane (MPS), and a subsequent reaction with 1,4-butyrolactone to create ion pairs in the polymer chain; meanwhile, the  $-\text{SO}_3\text{H}$  was produced by the oxidization of mercapto

group ( $-\text{SH}$ ) in the membranes. The effects of curing temperature on these membrane's performances were fully characterized. The results showed that the AIEC,  $\text{CIEC}_{\text{total}}$ , and  $\text{CIEC}_{\text{sulf}}$  of these three membranes coated once to thrice were in the range of 0.017–0.12, 0.1–0.53, and 0.029–0.14 mmol  $\text{g}^{-1}$ , respectively. The Coulombic repulsion between the molecular chains and the alternation of the speed of mass transfer to the ion exchange sites might be responsible for these behaviors. The measurement of water content revealed that it was independent of pH whether for the membranes coated once or twice. Pure water flux displayed a falling trend with the elevated coating times, which could be ascribed to the increase in the membrane thickness and the shrinkage of membrane pore size. The morphological observations of these membranes displayed that their microstructures could be affected by the curing temperature.

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